



# High-throughput study of the effects of inorganic additives and poisons on NH<sub>3</sub>-SCR catalysts. Part II: Fe-zeolite catalysts

P. Kern, M. Klimczak, T. Heinzelmann, M. Lucas, P. Claus\*

Department of Chemistry, Ernst-Berl-Institute/Chemical Technology II, Darmstadt University of Technology, Petersenstr. 20, D-64287 Darmstadt, Germany

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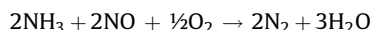
## ABSTRACT

This study was carried out to identify potential deactivating effects of inorganic materials which are put through an aftertreatment system of a diesel engine as combustion products of lubricant oil additives (i.e. Ca, Mg, Zn, P, B, Mo), impurities of (bio-)diesel fuel, urea solution (K, Ca) and aerosol particulate from intake air (Na, Cl). The effects of adding inorganic additives to an industrial Fe-MFI-SCR catalyst (Fe-BEA) have been evaluated by means of high-throughput methods. The results indicate the impact of different inorganic additives and poisons to Fe-zeolite-NH<sub>3</sub>-SCR catalysts in case of addition to the catalyst after catalyst preparation by ion exchange and molding of a washcoat by dip-coating procedures. Results of high-throughput screening are supplemented by experiments in more realistic scale, using catalysts and conditions close to the industrial application. As the mechanism of the uptake of inorganic poisons into the catalytic washcoat of an aftertreatment system is not yet quantitatively understood, thereby the addition of the additive to the as-sold catalyst was conducted in different ways, i.e. by wet-chemical impregnation and by exposure to aerosols generated from thermal decomposition of aqueous precursor solutions of potential poisons. It was found that alkaline metals, which are severe poisons to the established vanadia-based catalysts (see Part I), also exhibit deactivating potential towards Fe-zeolite catalysts and induce the reduction of the ammonia storage capability. However, their effect to the catalytic activity is dependant on the operation mode of the catalyst, and is far less pronounced than the effect of alkaline metals to vanadia-based catalysts. The exposure of Fe-zeolite catalysts to phosphates leads to a strong deactivation of the catalyst.

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## 1. Introduction

In the course of the introduction of the Euro IV and Euro V regulations, the selective catalytic reduction (SCR) of NO<sub>x</sub> by ammonia has, besides its existing application as method of choice for NO<sub>x</sub> removal in stationary emission sources, become a potential key technology for NO<sub>x</sub> removal in heavy duty truck vehicles. Contemporary NH<sub>3</sub>-SCR systems for removal of NO<sub>x</sub> in heavy duty truck vehicles do not contain a NO-oxidation catalyst and therefore work under standard-SCR conditions, making use of the reaction between nitrogen monoxide, ammonia and oxygen:



In the term of the use of vanadia-based NH<sub>3</sub>-SCR catalysts for NO<sub>x</sub> removal from exhaust gases of stationary emission sources for the past twenty years, the chemical deactivation of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> [1] and V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> [2–8] catalysts by the deposition of inorganic

poisons has been investigated in some detail by several groups. Different methods for the introduction of poisons have been applied, such as wet-chemical impregnation or incipient wetness procedures [2–5], controlled exposure to aerosols of potential poisons [6,7] and exposure to exhaust streams generated by burning poison-enriched fuel in furnaces upstream from the catalyst [8]. Furthermore field studies from power plants [9] and mobile emission sources [10] combined with a chemical analysis of aged catalysts add to the knowledge, though the assessment of the impact by chemical poisoning respectively by single poisons is highly difficult in these cases.

The established vanadia-based catalysts are, especially in the field of mobile emission sources, about to be partly substituted by Fe-zeolite catalysts for NH<sub>3</sub>-SCR due to better high-temperature performance and non-toxicity.

Published aging studies concerning zeolite-based NH<sub>3</sub>-SCR catalysts have mainly covered the hydrothermal stability of the materials [11,12]. Dealumination of the zeolite at temperatures higher than 600 °C resulting in reduced acidity of the zeolite framework, clustering of Fe-species of low molecularity and/or pore plugging by alumina has been found to be a major cause for deactivation. However, if, as is the case in current heavy duty

\* Corresponding author. Tel.: +49 6151 16 5369/4788; fax: +49 6151 16 4788.  
E-mail address: [claus@ct.chemie.tu-darmstadt.de](mailto:claus@ct.chemie.tu-darmstadt.de) (P. Claus).

applications, a  $\text{NH}_3$ -SCR DeNO<sub>x</sub> system is not positioned in close vicinity to a particulate filter which requires thermal regeneration, temperatures as high as 600 °C are barely reached at the DeNO<sub>x</sub> catalyst of a heavy duty vehicle. To our knowledge, only very few studies concerning the impact of inorganic poisons to the performance of zeolite-based  $\text{NH}_3$ -SCR catalysts have been published in the literature so far. Silver et al. [13] recently published a study where honeycomb Fe-zeolite-SCR catalysts were exposed to 10 g/L phosphorous from the downstream combustion of diesel fuel enriched with tricresyl phosphate and found a significant and nearly linear correlation between catalytic activity and phosphorous uptake. No significant activity differences between catalysts aged in sulphur rich and sulphur free exhaust gases were detected. van Kooten et al. [14] conducted comparative aging experiments of a Ce-ZSM-5-based SCR catalyst mounted behind a diesel engine and in a synthetic exhaust gas free of inorganic impurities and particulate matter. At comparable aging conditions, a stronger deactivation of the catalyst aged with real exhaust gas was observed. This was attributed to inorganic (Zn, P, S, Ca) and carbonaceous deposits on the catalyst surface, which accumulated in spite of the presence of a wall-flow particulate filter upstream of the SCR catalyst. The laboratory post-mortem analysis of an engine-aged (120,000 Miles) Cu-zeolite-based  $\text{NH}_3$ -SCR catalyst by Cheng et al. [15] also showed a significant adhesion of phosphorous, zinc and calcium. Qi et al. [16] conducted a field study at a coal fired power plant in the United States. They were able to use relative pseudo-first order rate constants determined by the investigation of chemically poisoned  $\text{V}_2\text{O}_5/\text{TiO}_2$  catalysts to predict the long term deactivation of a Fe-La-ZSM-5 zeolite in dependence of the accumulation of poisons. This may suggest very similar deactivating effects of inorganics to vanadia-based catalysts and Fe-zeolites and was justified by the similar chemical mechanisms discussed for  $\text{NH}_3$ -SCR on  $\text{V}_2\text{O}_5$ - $\text{WO}_3/\text{TiO}_2$  (as defined by the Topsoe model [17]) and Fe-zeolite catalysts.

The previously mentioned studies concerning the chemical deactivation of vanadia-based catalysts have identified metals with alkaline character as strongest poisons [1–8]. According to Long and Yang [18] and Devadas et al. [19] the major difference to the Topsoe model [17] in the chemical mechanism of  $\text{NH}_3$ -SCR over Fe-zeolites is the required direct adsorption of NO on  $\text{Fe}^{3+}$  centers of low molecularity and its partial oxidation to  $\text{NO}_2$ . Ammonia bound to Brønstedt- or Lewis-acidic centers then reacts with these  $\text{NO}_x$  species to form nitrogen. Kumar [20] and Long and Yang [21] both found a correlation of the zeolites framework acidity and the Si/Al ratio to the catalytic activity of Fe-zeolites, if the distribution of Fe-species of different molecularity in the framework was comparable. In that terms it seems reasonable to expect a similar impact of inorganic poisons to Fe-zeolites and vanadia-based catalysts. However, pore plugging phenomena by free poisons not reacting with the zeolite framework or narrowing of the pore system may have a more severe impact in case of the use of a microporous material. The data presented in this work allows for the assessment of the poisoning potential of different inorganic compounds to Fe-zeolite catalysts and for a comparison to literature data concerning the established vanadia-based materials for  $\text{NH}_3$ -SCR. The effects of inorganic additives and poisons on  $\text{V}_2\text{O}_5$ - $\text{WO}_3/\text{TiO}_2$  catalysts are presented in a Part I.

## 2. Experimental

### 2.1. Catalysts

Fe-zeolite powder with high Fe-content (Fe-MFI and Fe-BEA; 5.5 wt.%  $\text{Fe}_2\text{O}_3$ , Si/Al = 25–27) has been provided by “Südchemie

AG”, and is supposed to be close to industrially applied material. Ceramic honeycombs (cordierite, cell density: 72 cpsi in case of high-throughput experimentation, 400 cpsi in case of catalytic tests close to industrial conditions) have been coated with the powder making use of a dip-coating procedure as described by Nijhuis et al. [22] (2 wt.% colloidal  $\text{SiO}_2$  (Ludox AS 30) with respect to the mass of the zeolite used as binder). Zeolite contents have been adjusted to 90 g/L in case of 400 cpsi honeycombs, zeolite contents of 30–45 g/L have been used for high throughput investigations.

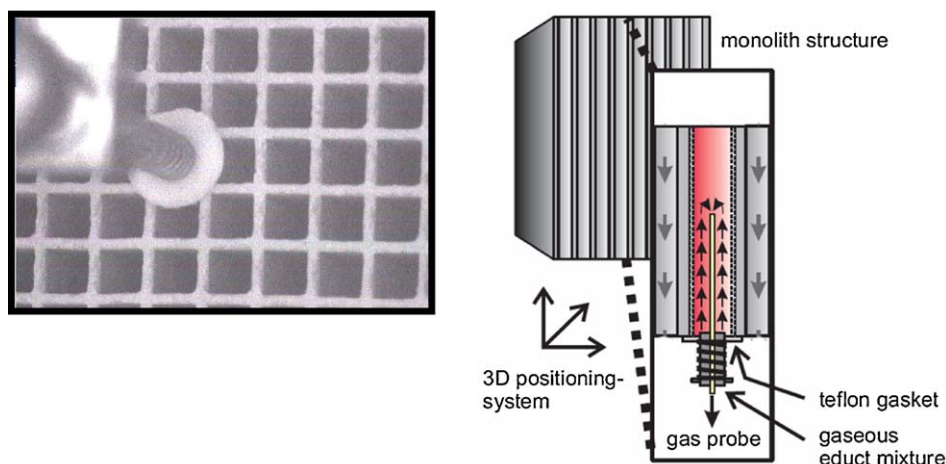
### 2.2. Catalytic investigation of poisoned zeolite catalysts by high-throughput experimentation

Due to an experimental matrix of more than 3000 experiments not only covering the Fe-zeolite catalyst discussed here, we applied high-throughput technology to the screening of inorganic poisons. The methodology developed and applied was supposed to stay as close to the reaction geometrics of automotive exhaust catalysis as possible, and therefore makes use of ceramic honeycombs made of gas proof material (60 mm × 30 mm × 75 mm, Cordierite 410, 200 channels, Inocerme) with a channel density of 72 cpsi. The single channels of the honeycomb are uniformly coated with the Fe-zeolite and can be treated as independent plug flow reactors. The principle of this “multichannel reactor” for high throughput applications in the field of automotive exhaust catalysis has been described in detail elsewhere [23]. Each individual channel can be modified by inorganic additives by the use of an automated pseudo-incipient wetness procedure, which is conducted by a pipetting robot (Tecan Miniprep 60). The procedure consists of the filling of a channel with an aqueous precursor solution of the desired additive, with concentrations derived from the apparent water adsorption capacity of the coating. To prevent any enrichment of the additive on the catalyst surface, the solution is being sucked off from the channel after 2 s.

The newly developed apparatus for SCR conditions allows the catalytic investigation of single channels of this reactor system in a quasi simultaneous channel by channel procedure. The core of the high-throughput screening device is a 3D positioning system which enables the placement of a gas dosing and sampling unit inside of single channels of a 72-cpsi honeycomb. Fig. 1 provides a schematic representation of the sampling and dosing system and allows for an assessment of the measurement principle in high throughput geometrics. A more detailed description of the apparatus, the measurement procedure and the proof of principle can be found in the literature [23,24]. Doseable gases are NO,  $\text{NH}_3$ , CO,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , air and nitrogen. The operation temperature window is room temperature to 450 °C and gas hourly space velocities (GHSV) of 10,000–200,000  $\text{h}^{-1}$  with respect to the volume of an individually coated plug flow reactor can be applied. The equipment allows the catalytic screening of 128 differently modified Fe-zeolite-SCR catalysts in approximately 20 h. On-line FTIR analysis provides rapid analysis of the reaction products, the measurement time of a single catalyst is 8 min due to a compromise between reasonable analysis time and accuracy, as the initial activity of an SCR catalyst is being influenced by ammonia storage phenomena.

### 2.3. Catalytic investigation of segments of industrial serial catalysts and corresponding poisoning procedures

Block shaped segments (150 mm × 10 mm × 10 mm, 7 × 7 channels) were cut out of serial catalysts (VWT, 1 L, 400 cpsi, 200 g/L washcoat, cordierite) or of honeycombs representing a serial catalyst as close as possible (Fe-MFI zeolite, 1 L, 400 cpsi,



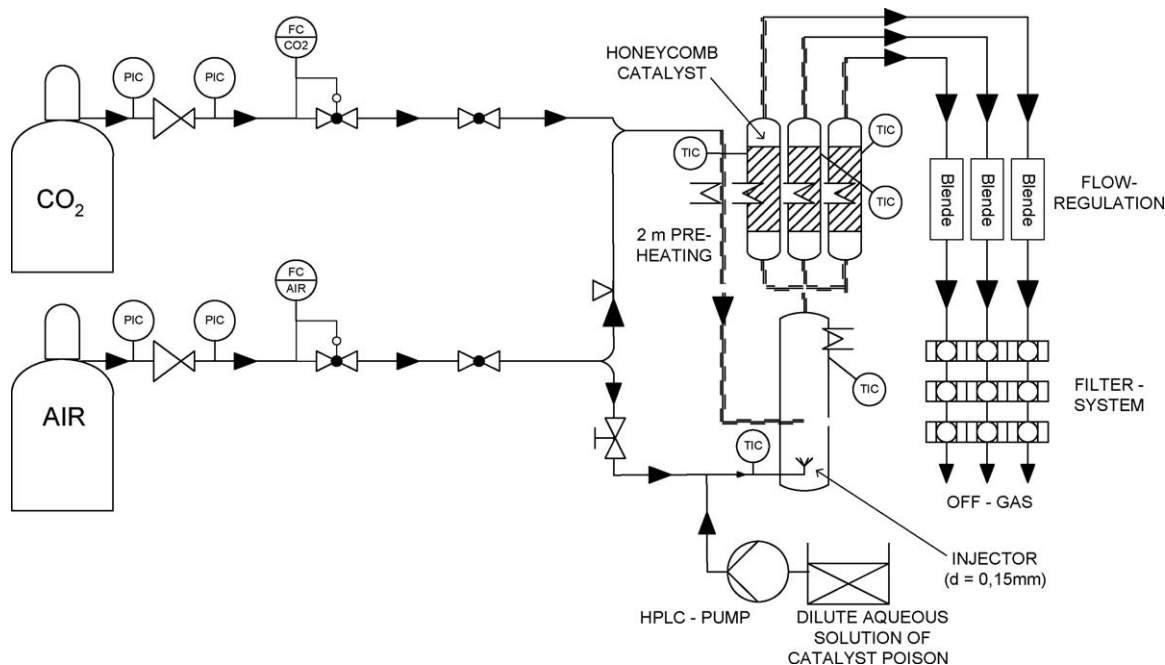
**Fig. 1.** Principle of gas dosing and probe sampling in high-throughput experiments by placement of a sniffle device in a single channel of a washcoated monolith (left) which has previously been individually modified by an impregnation procedure (right).

90 g/L washcoat, cordierite). The segments were calcined in air (24 h, 550 °C) prior to any catalytic investigation, different specimen of the same catalyst type showed comparable activities thereafter. Catalytic testing of these specimens was conducted in a laboratory flow reactor at a GHSV of 50,000 h<sup>-1</sup>. The composition of the synthetic exhaust gas was 1000 vppm NO, 0–1200 vppm NH<sub>3</sub>, 1000 vppm CO, 5. vol.% CO<sub>2</sub>, 8 vol. % O<sub>2</sub>, 5. vol.% H<sub>2</sub>O and balance nitrogen. Activity curves were recorded at four to eight temperatures between 175 and 450 °C, the feed ratio  $\alpha = \text{NH}_{3,\text{in}}/\text{NO}_{\text{in}}$  was varied stepwise between 0.2 and 1.2 at each temperature to obtain ammonia slip–DeNO<sub>x</sub> curves. Inorganic additives respectively poisons were introduced by short-time aqueous impregnation (10 s) or by exposure to aerosols generated from the thermal decomposition of low concentrated aqueous precursor solutions. The latter procedure was conducted in the apparatus depicted in Fig. 2. The combined hydrothermal aging and poisoning was carried out over 50 h. Thereby, aerosols of inorganic particulate or inorganic gaseous compounds are being preformed by spraying a dilute precursor solution into an evaporation chamber, the carrier gas is then equally divided into three streams

and set through three different honeycomb catalysts in parallel. The carrier gas was air and 5 vol.% H<sub>2</sub>O, the temperature at the catalyst 500–550 °C and GHSV = 50,000 h<sup>-1</sup>.

#### 2.4. Analysis of reaction gases and expression of results

The analysis of the reaction products was conducted by high resolution FTIR spectroscopy (Thermo Nicolet Antaris IGS). The volume of the gas cell is 200 mL, the volume flow through the cell is 220 mL/min in case of high throughput investigation and 500 mL/min in case of the investigation of segments of industrial serial catalysts. All lines from heated reaction zones to the analysis are being held at a temperature of 180 °C to avoid any formation of solid ammonium nitrate. The detection accuracies of NO, NH<sub>3</sub>, CO, N<sub>2</sub>O and NO<sub>2</sub> are estimated to be 5 ppm or better. Assuming the 1:1 stoichiometry of the standard-SCR reaction, nitrogen balances of experiments with VWT-SCR catalysts are closed within 5% in case of high-throughput testing and within 2% in case of catalytic tests of segments of industrial serial catalysts. With Fe–zeolites, a slight over-consumption of ammonia ( $\text{NH}_{3,\text{consumed}}/\text{NO}_{\text{consumed}} = 1.02\text{--}1.1$ ,



**Fig. 2.** Principle of gas-phase poisoning of 400 cpsi honeycomb catalysts.

depending on experimental conditions) has been detected. This has been reported in the literature [25] before.

The nitrogen yield (DeNOx %) has been calculated from the analytical data by Eq. (1):

$$\text{DeNOx (\%)} = \frac{\text{NO}_{\text{in}} - (\text{NO}_{\text{out}} + \text{NO}_{2,\text{out}} + \text{N}_2\text{O}_{\text{out}})}{\text{NO}_{\text{in}}} \times 100 \quad (1)$$

As activities of non-poisoned specimen for high-throughput investigations, which appeared to be coated identically, varied slightly and, thus, results of high-throughput experiments as relative DeNOx values are given.

Selectivities of the conversion of NO ( $S_{\text{NO}}$ ) and  $\text{NH}_3$  ( $S_{\text{NH}_3}$ ) to nitrogen were obtained by dividing the DeNOx value ( $\text{N}_2$  yield) through the conversion  $X_{\text{NO}}$  or  $X_{\text{NH}_3}$ .

### 2.5. Catalyst characterization by temperature-programmed desorption (TPD) of $\text{NH}_3$ and $\text{NO}_2$ , physisorption of nitrogen, UV-vis-DRS, temperature-programmed reduction (TPR) with hydrogen

Chemisorption of  $\text{NH}_3$  and  $\text{NO}_2$  has been investigated by temperature-programmed desorption of ammonia and nitrogen dioxide. Powder catalysts were pretreated in air (550 °C, 24 h), then transferred to a quartz glass laboratory flow reactor (75 mg catalyst, 500 mg SiC) and additionally dried for 2 h at 300 °C. The powder reactor is equipped with a stainless steel heating jacket. Saturation of the catalyst powder was carried out at 50 °C (1 vol.%  $\text{NH}_3/\text{N}_2$ ; 0.2 vol.%  $\text{NO}_2/\text{synthetic air}$ , 450 mL/min, 2 h). Physisorbed species were removed by flushing with nitrogen at 150 °C, and desorption of chemisorbed species was monitored dynamically under nitrogen flow (450 mL/min, 10 K/min, 150–525 °C) by FTIR spectroscopy. Total  $\text{NH}_3/\text{NO}_2$  storage capacities were obtained by integration of the  $\text{NH}_3/\text{NO}_2$  concentration profile. UV-vis spectra in diffuse reflexion were obtained with a Cary 100 spectrometer (Varian Inc.). Spectra were recorded in the range between 200 and 800 nm at room temperature with a rate of 200 nm/min, using the H-form of the zeolite as reference. Exploratory analysis of the active surface by  $\text{N}_2$  physisorption was conducted with an analyser Autosorb 3B (Quantachrome), specimens were dried at 150 °C vacuum before analysis. Despite the limitations of  $\text{N}_2$  physisorption for detection of specific surface area and pore structures of zeolites, comparative data can be used for the qualitative assessment of the effects of inorganic additives to the materials.

## 3. Results

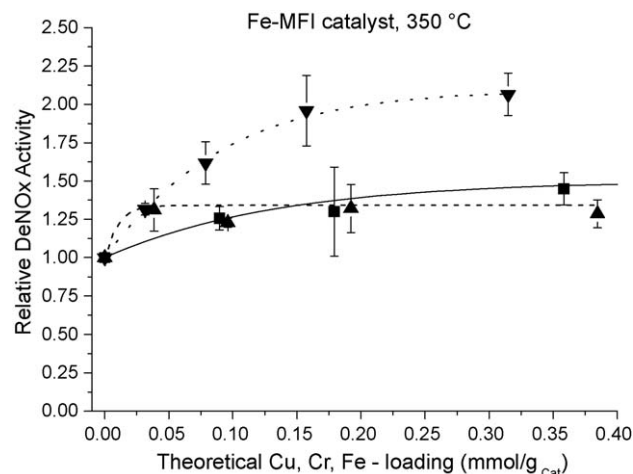
### 3.1. Activity of undoped catalysts in high-throughput experiments

The catalytic properties of all non-poisoned Fe-zeolite catalysts (8 repetitions) are summarized in Table 1. The high-temperature activity of a Fe-MFI zeolite with a thinner coating was significantly larger than the high-temperature activity of a Fe-BEA specimen with a thicker coating. The difference should not only be attributed to material properties but probably may also be influenced by properties of the catalytic coating (for example, surface/volume ratio, coating density), which, due to the applied basic dip-coating methodology, could not be controlled in detail.

**Table 1**  
Activity of undoped Fe-zeolite catalysts in high-throughput experiments<sup>a</sup>.

Catalyst, washcoat (g)	T (°C)	NO conversion unpoisoned cat.	DeNOx unpoisoned cat.	$S_{\text{NO}}$	$S_{\text{NH}_3}$
Fe-BEA (45 g/L)	350	28.5 ± 2%	26 ± 2%	94 ± 2%	81 ± 8%
Fe-BEA (45 g/L)	450	58 ± 4%	56 ± 4%	98 ± 2%	79 ± 8%
Fe-MFI (30 g/L)	350	30 ± 4%	27 ± 4%	95 ± 2%	81 ± 5%
Fe-MFI (30 g/L)	450	76 ± 7%	73 ± 7%	99 ± 1%	92 ± 2%

<sup>a</sup> 1000 vppm NO, 1000 vppm  $\text{NH}_3$ , 1000 vppm CO, 5 vol.%  $\text{CO}_2$ , 5 vol.  $\text{H}_2\text{O}$ , 8 vol.  $\text{O}_2$ ,  $\text{N}_2$ ; GHSV = 50,000 h<sup>-1</sup>.



**Fig. 3.** Activation of Fe-MFI catalyst by impregnation with: (▼)  $\text{Cu}(\text{NO}_3)_2$ , (▲)  $(\text{NH}_4)_2\text{CrO}_4$ , (■)  $\text{Fe}(\text{NO}_3)_3$ ; 350 °C; 1000 vppm NO, 1000 vppm  $\text{NH}_3$ , 1000 vppm CO, 5 vol.%  $\text{CO}_2$ , 5 vol.%  $\text{H}_2\text{O}$ , 8 vol.%  $\text{O}_2$ ,  $\text{N}_2$ ; GHSV = 50,000 h<sup>-1</sup>.

Relative DeNOx activities of identically poisoned catalysts showed, at a specific temperature of investigation, comparable values (deviation: <5%) in spite of not completely identical properties of the coating.

### 3.2. Additives with activity promoting effect on Fe-zeolite catalysts in high-throughput experiments

The industrial Fe-MFI and Fe-BEA catalysts with high Fe-loading (5.5 wt.%) were promoted by impregnation with  $\text{Cu}(\text{NO}_3)_2$  and  $(\text{NH}_4)_2\text{CrO}_4$ . Furthermore the introduction of additional Fe(III)-species resulted in a higher DeNOx activity (Fig. 3) in high-throughput experiments.

In case of the MFI-zeolite, strong activity increasing effects were detected at lower temperatures (lower conversions) of up to 350 °C only. At an investigation temperature of 450 °C, only slight activity promotion was observable. This indicates that in the reaction geometry of the multichannel reactor, the rate of conversion of the non-poisoned Fe-MFI catalyst is controlled by mass transport at 450 °C. The strong activity increasing effect of the introduction of Cu(II)-ions by impregnation with Cu(II)nitrate was monitored with the Fe-MFI sample only. Cu-zeolites are known for their tendency to produce the greenhouse gas  $\text{N}_2\text{O}$  [26] under  $\text{NH}_3$ -SCR conditions. The post-synthesis impregnation of Fe-zeolites both with Cu(II)nitrate and  $(\text{NH}_4)_2\text{CrO}_4$  resulted in an increased production of  $\text{N}_2\text{O}$ . In case of the impregnation with Cu(II)nitrate, in the HC-free synthetic emission gas used here, this effect was observable in very small scale only (Table 2).

High-throughput data concerning the selectivity decreasing effects of chromium and copper to Fe-MFI zeolites were scaled up by experiments with 400 cpsi honeycomb catalysts closer to industrial application. Chromium and copper precursors were decomposed thermally upstream of the catalyst and put through the honeycomb in form of inorganic particulate. The total throughput of poisons was 3 mmol Cr/Cu during 50 h as described



**Table 2**Effect of chromium and copper addition to Fe–MFI catalysts in selected high-throughput experiments<sup>a</sup>.

Catalyst	Y <sub>N<sub>2</sub></sub> (%)		S <sub>NO</sub> (%)		S <sub>NH<sub>3</sub></sub> (%)		N <sub>2</sub> O (vppm)	
	350 °C	450 °C	350 °C	450 °C	350 °C	450 °C	350 °C	450 °C
Fe–BEA (45 g/L)	26 ± 2	56 ± 2	92	98	84	80	9	10
Fe–BEA/2 wt.% Cu	30 ± 3	58 ± 4	91	95	88	75	16	23
Fe–BEA/2 wt.% Cr	28	62 ± 1	88	89	71	63	28	68
Fe–MFI (30 g/L)	30 ± 4	76 ± 7	95	98	81	92	10	9
Fe–MFI/2 wt.% Cu	62 ± 8	79 ± 3	96	97	91	85	14	20
Fe–MFI/2 wt.% Cr	39 ± 3	82 ± 1	95	96	85	87	15	26

<sup>a</sup> 1000 vppm NO, 1000 vppm NH<sub>3</sub>, 1000 vppm CO, 5 vol.% CO<sub>2</sub>, 5 vol.% H<sub>2</sub>O, 8 vol.% O<sub>2</sub>, N<sub>2</sub>; GHSV = 50,000 h<sup>−1</sup>.

above, the final poison content (equal mixture of material from different axial positions) was 0.6 wt.% Cr (ca. 5% of throughput) and 0.15 wt.% Cu (ca. 1% of throughput).

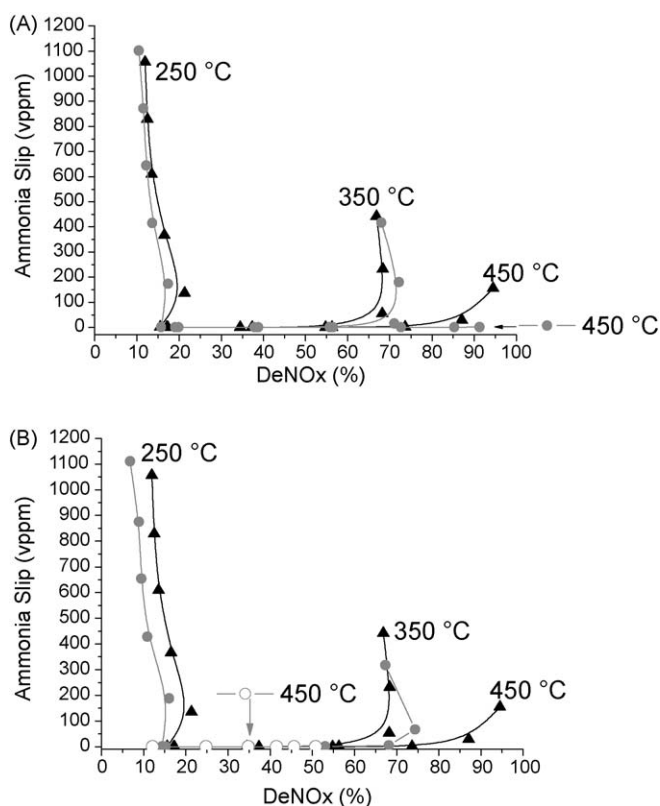
As shown in Fig. 4, the ammonia oxidation activity of both the copper- and chromium aerosol-treated catalyst increased in an amount not observed in high-throughput experiments, where copper and chromium were introduced into the zeolite washcoat by a wet-chemical method. As specified above, results of catalytic testing of non-high-throughput experiments (i.e. Fig. 4, aerosol poisoning) are given as ammonia slip–DeNO<sub>x</sub> curves (variation of  $\alpha = \text{NH}_{3,\text{in}}/\text{NO}_{\text{in}}$ : 0.2–1.2), which allows for an interpolation to conditions comparable to the operating mode in an automobile, where ammonia feed is regulated with respect to an ammonia slip value not higher than about 10–25 vppm. The DeNO<sub>x</sub> activity (at  $\alpha = 1.2$ ) which is maximally achievable with the chromium poisoned catalyst decreased to 51% due to ammonia oxidation at 450 °C and  $\alpha = 1.2$ . This corresponds to a drop of selectivity of

ammonia conversion to nitrogen from 90% (unpoisoned catalyst) to 43%. It is known from the literature, that clustered iron oxides as present in over-exchanged Fe–zeolites increase the ability of the material to oxidise ammonia to nitrogen [27]. Clustered copper- and chromium-containing phases as potentially present in the aerosol poisoned substrates seem to exhibit this effect even more pronounced. The impact of oxidised particulate from motor abrasion should be considered as a potential source if a decrease of NH<sub>3</sub>-selectivity is observed over the lifetime of a zeolitic SCR catalyst. The formation of N<sub>2</sub>O was evident in case of aerosol poisoning also, but only in small scale, as observed in high-throughput experiments with chromium and copper poisoned Fe–MFI zeolites.

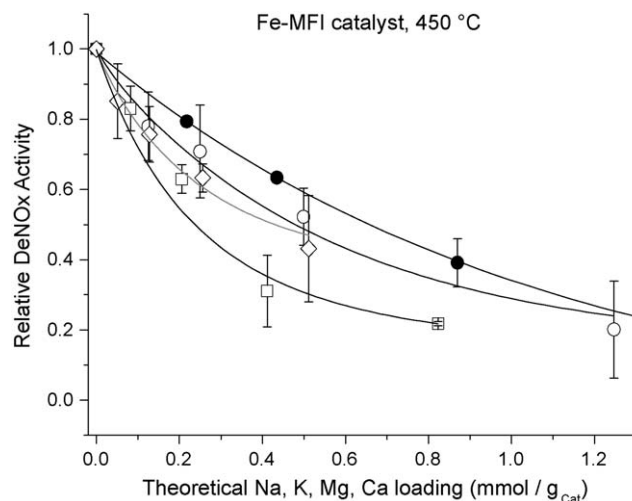
### 3.3. Additives with deactivating effect on Fe–zeolite catalysts in high-throughput experiments: alkaline- and earth alkaline-metals

In case of the addition of alkaline- or alkaline earth-metals to honeycomb Fe–zeolite-based SCR catalysts by impregnation or exposure to aerosols, all investigated additives (K, Na, Mg, Ca) showed strong deactivating potential (Fig. 5).

Studies in the literature indicate, as described above, that the basicity (EN, stabilisation of surface hydroxyl groups by electron withdrawal) of alkaline metals and alkaline earth metals is an appropriate descriptor for their poisonous impact on vanadia-based NH<sub>3</sub>-SCR catalysts. This could be visualized straightforward by the high throughput technique used here, thereby verifying existing literature data [28]. The corresponding order of poison strength to the vanadia-based catalyst is K > Na > Ca > Mg, which does not comply with the data derived with Fe–zeolites,



**Fig. 4.** Gas-phase poisoning of 400 cpsi Fe–MFI zeolite (90 g/L) honeycomb catalysts; (▲) Fe–MFI catalyst hydrothermally treated (550 °C, 5 vol.% H<sub>2</sub>O, air, 50 h, GHSV = 50,000 h<sup>−1</sup>); (●) Hydrothermal treatment + exposure to 3 mmol Cr or Cu from thermal decomposition of: Cu(NO<sub>3</sub>)<sub>2</sub> (Cu content 0.2 wt.%, A) or (NH<sub>4</sub>)<sub>2</sub>CrO<sub>4</sub> (Cr content 0.6 wt.%, B), 1000 vppm NO, 1000 vppm NH<sub>3</sub> ( $\alpha = 0.2, 0.4, 0.6, 0.8, 1, 1.2$ ), 1000 vppm CO, 5 vol.% CO<sub>2</sub>, 5 vol.% H<sub>2</sub>O, N<sub>2</sub>, GHSV = 50,000 h<sup>−1</sup>.



**Fig. 5.** Deactivation of Fe–MFI catalysts by impregnation with (●) NaNO<sub>3</sub>, (◇) KNO<sub>3</sub>, (□) Mg(NO<sub>3</sub>)<sub>2</sub>, (○) Ca(NO<sub>3</sub>)<sub>2</sub>; 1000 vppm NH<sub>3</sub>, 1000 vppm CO, 5 vol.% CO<sub>2</sub>, 5 vol.% H<sub>2</sub>O, N<sub>2</sub>, GHSV = 50,000 h<sup>−1</sup>.

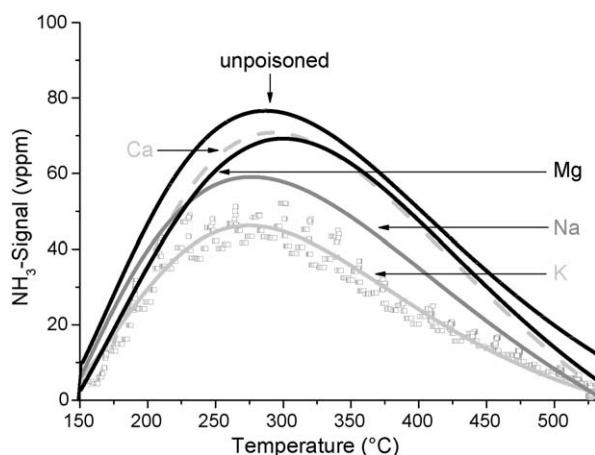


Fig. 6.  $\text{NH}_3$  temperature-programmed desorption profiles of poisoned Fe-MFI catalysts.

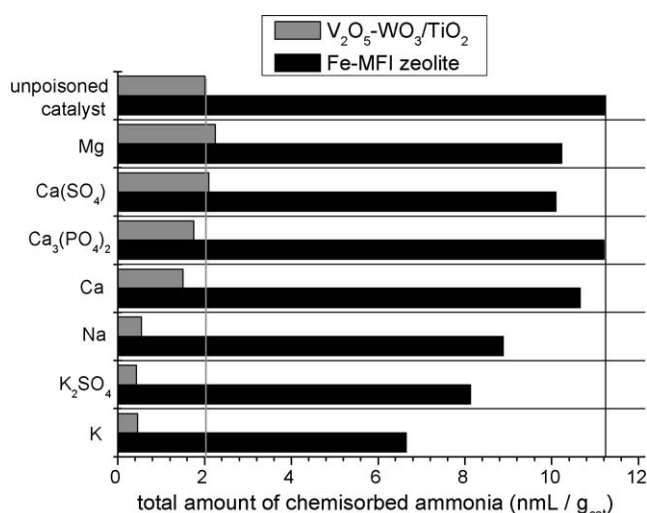


Fig. 7. Integral ammonia storage capacity of Fe-MFI catalysts in comparison to as treated standard  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalysts [24].

where magnesium is the most severe poison ( $\text{Mg} > \text{K} \approx \text{Ca} > \text{Na}$ ). The impact of poisoning Fe-MFI zeolites with alkaline metals and alkaline earth metals to the amount of ammonia chemisorbed by the material has been evaluated by TPD (Figs. 6 and 7) and compared to the effect to a commercial  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalyst. Hereby, as the active material was not separable from the ceramic honeycombs used for activity tests, powder catalysts impregnated with 0.3 mmol/g of each poison were used.

Exploratory activity measurements with the poisoned powder catalysts in  $\text{H}_2\text{O}$ - and  $\text{CO}_2$ -free synthetic exhaust gas at  $\alpha = 1$  confirmed the strong deactivating effect of calcium and magne-

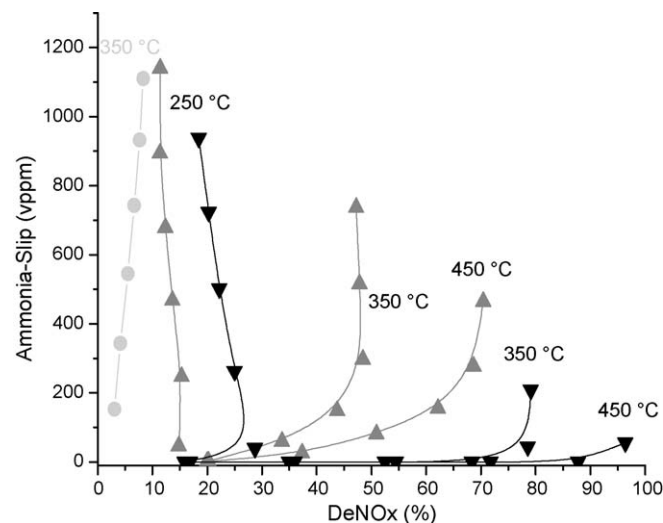


Fig. 8.  $\text{NH}_3$  slip-DeNOx curves of a 400 cpsi Fe-MFI zeolite (90 g/L) honeycomb catalyst poisoned by impregnation with  $\text{KNO}_3$  to contain 0.3 mmol K/g washcoat, direct comparison to a standard  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalyst with exactly the same treatment ([24]); ( $\blacktriangledown$ ) Fe-MFI catalyst impregnated with water, then thermally treated; ( $\blacktriangle$ ) Fe-MFI catalyst impregnated with aqueous  $\text{KNO}_3$ -solution to contain 0.3 mmol K/g washcoat; ( $\bullet$ )  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalyst impregnated with aqueous  $\text{KNO}_3$ -solution to contain 0.3 mmol K/g washcoat, 1000 vppm NO, 200–1200 vppm  $\text{NH}_3$  ( $\alpha = 0.2, 0.4, 0.6, 0.8, 1, 1.2$ ), 1000 vppm CO, 5 vol.%  $\text{CO}_2$ , 5 vol.%  $\text{H}_2\text{O}$ ,  $\text{N}_2$ , GHSV = 50,000  $\text{h}^{-1}$ .

sium, but different to experiments with honeycomb catalysts, only minor activity losses were observed with fine-powdered ( $d_{\text{Grain}} = 100 \text{ nm} - 10 \mu\text{m}$ ) Na- and K-poisoned catalysts (Table 3).

Under reaction conditions, the relative  $\text{NH}_3$  surface coverage of an SCR catalyst is a function of the ammonia feed concentration, and if the rate of the reaction is merely decreased by a reduced ammonia adsorption constant, a strong dependence of the poisoned catalysts activity from the feed ratio  $\text{NH}_3/\text{NO}$  is to be expected. In fact, severely potassium poisoned  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  catalysts have been reported not to reach their maximum DeNOx activities until  $\text{NH}_3$ -slip values of 12,000 vppm and higher [5].

Fig. 8 shows the ammonia slip-DeNOx curves of a Fe-MFI-SCR 400 cpsi honeycomb catalyst which was doped with 0.3 mmol K/g washcoat by wet-chemical impregnation. At 350 °C, where ammonia inhibition is not observed, the non-poisoned catalyst reaches its maximum DeNOx activity at ammonia slip values below 100 vppm, while the reaction rate of the poisoned catalyst seems to be independent of the ammonia feed rate at ammonia slip values of 300–400 vppm.

Thus, the activity losses of the poisoned catalyst should only be partly attributed to the loss of ammonia storage capacity. Note that a VWT-catalyst was, in coincidence with high-throughput evaluation, rendered near to inactive by the same molar concentration of potassium. Table 3 gives an overview over further characterization data of potassium and calcium containing Fe-MFI catalysts.

Table 3

Characterization data of Fe-MFI zeolites poisoned with  $\text{KNO}_3/\text{Ca}(\text{NO}_3)_2$ .

Catalyst: Fe-MFI	$T_{50,\text{NO}}$ (°C) <sup>a</sup>	UV-vis-DRS: relative signal intensity $I/I_{\text{total}}$			N <sub>2</sub> physisorption	
		<400 nm	400–500 nm	>500 nm	BET surface <sup>b</sup> (m <sup>2</sup> /g)	Micropore surf. area <sup>b</sup> (m <sup>2</sup> /g)
Unpoisoned	290	0.29	0.34	0.37	308	525
0.3 mmol K/g <sup>c</sup>	295	0.33	0.34	0.33	268	<404
0.3 mmol Ca/g <sup>c</sup>	320	0.32	0.35	0.33	295	<480

<sup>a</sup> Quartz glass laboratory flow reactor, packed bed, 75 mg catalyst ( $d_{\text{Grain}} = 100 \text{ nm} - 10 \mu\text{m}$ ), 500 mg SiC, volume flow: 700 mL/min, 1000 vppm NO, 1000 vppm  $\text{NH}_3/7 \text{ vol.}\%$   $\text{O}_2$ ,  $\text{N}_2$ .

<sup>b</sup> N<sub>2</sub> physisorption, BET analysis and Horvath-Kavazoe analysis.

<sup>c</sup> Incipient wetness using water or aq. precursor solution (nitrates) of the poison to contain 0.3 mmol/g K/Ca; then calcined in air (550 °C/24 h).

UV–vis spectroscopy in diffuse reflectance was used to determine any changes of the dispersity of Fe-species due to poisoning Fe-zeolite catalysts with inorganic additives. Thereby,  $O \rightarrow Fe^{3+}$  ligand to metal charge-transfer transitions in the UV region  $<400$  nm have been ascribed to highly active Fe-species of low molecularity and d–d transitions in the region of 400–500 nm and, respectively,  $>500$  nm, mainly indicate the occurrence of iron nanoparticles and large, potentially inactive hematite clusters [20]. As assessable by the results of UV–vis analysis (spectrum given in combination with data to phosphorous poisoning, Chapter 3.4), doping zeolites with alkaline metals did not induce clustering of any Fe-species of low molecularity, but resulted in a stabilization of potentially active species in comparison to the as-treated non-poisoned catalyst, a phenomena that has been described earlier [11]. Furthermore, no influence on the reducibility of Fe-species was detectable by temperature-programmed reduction with hydrogen (see Chapter 3.4). Exploratory assessment of the active surface of poisoned catalysts was conducted using physisorption of nitrogen (Table 3). In combination with corresponding data of the unpoisoned catalyst, the methodology can be applied for comparative analysis, in spite of the known limitations in accuracy due to capillary condensation phenomena. Doping with calcium and, even more pronounced, with potassium resulted in a decrease of micropore and BET surface area, so partial plugging of micropores and of inter-grain mesopores, the latter being of importance for an effective transport of reactants into the deeper layers of a structured zeolitic washcoat, seemed to apply.

Due to the characterization data and to the activity measurements with honeycomb and fine-powdered catalysts we ascribe activity losses by poisoning Fe-MFI zeolites with alkaline metals to pore plugging by free poisons in the form of oxides or carbonates and to minor losses of ammonia storage capacity due to the uptake of potassium or sodium on cationic positions. The latter phenomena also results in narrowing of the average micropore radius and induces further mass-transport limitation. The overall deactivating effect of alkaline metals and alkaline earth metals was also observed using aerosol methods for K-, Na- and Ca-poisoning (not shown here).

### 3.4. Additives with deactivating effect on Fe-zeolite catalysts in high-throughput experiments: zinc, phosphates and borates

A major source of potential inorganic poisons put through a diesel exhaust aftertreatment system is the lubrication oil additive ZDDP (zinc alkyl dithiophosphates), used for wear protection by the formation of tribochemical films on surfaces in contact. It can be partly replaced by boron containing additives in order to reduce phosphorous content of lubrication oils. As shown in Fig. 9, the wet-chemical addition of phosphates [as  $(NH_4)_2HPO_4$ ], zinc [ $Zn(NO_3)_2$ ] and borates [ $H_3BO_3$ ] to Fe-zeolite-based SCR catalysts resulted in strong deactivation in high-throughput testing of the materials.

A deactivating effect by impregnation of an automotive catalyst with phosphates is to be expected. During calcination, condensation to polyphosphoric acids and polyphosphates with low vapour pressures with the formal final product of polymeric  $P_2O_5$  prevents loss of phosphorous. The formation of glassy polyphosphates in coincidence with the blockage of active sites is a known deactivation mechanism in case of 3-way catalysts [29]. The deactivation of Fe-MFI catalysts by zinc and phosphorous could also be demonstrated by poisoning 400 cpsi honeycombs from the gas phase (Fig. 10). Here, the poisons were presumably put through the catalyst in form of gaseous phosphoric acid and, respectively, zinc oxide fumes. Only minor deactivation by Zn was imminent, as only low amounts of Zinc were retained at the catalyst.

As shown in Table 4, a Fe-MFI powder catalyst, which was impregnated with zinc nitrate to contain 0.3 mmol Zn, showed

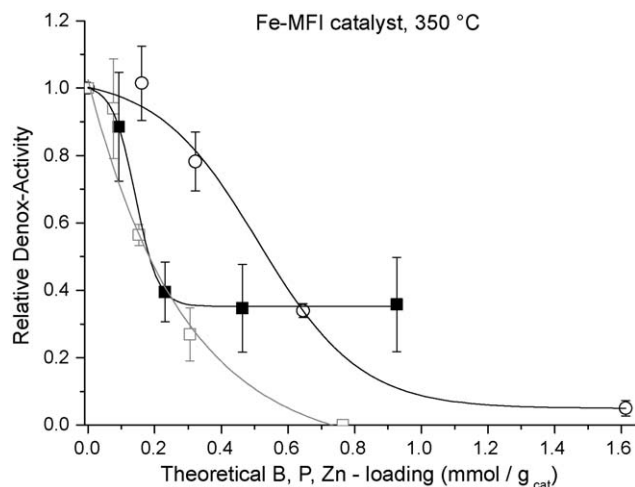


Fig. 9. Deactivation of Fe-MFI SCR catalyst by impregnation: (■)  $H_3BO_3$ , (○)  $(NH_4)_2HPO_4$ , (□)  $Zn(NO_3)_2$ ; 350 °C; 1000 vppm NO, 1000 vppm  $NH_3$ , 1000 vppm CO, 5 vol.%  $CO_2$ , 5 vol.%  $H_2O$ , 8 vol.%  $O_2$ ,  $N_2$ ; GHSV = 50,000  $h^{-1}$ .

severe loss of active surface. No loss of ammonia storage capacity was detected.

While phosphate poisoned catalysts showed only minor decrease of ammonia adsorption capability, the chemisorption of nitrogen dioxide decreased strongly with growing phosphorous content. While this could be justified by pure pore plugging and acid properties of polyphosphoric acids, ion exchange resins containing oligomeric Fe-species of low molecularity can be used for the removal of phosphates from aqueous solution [30]. In the UV–vis-DRS spectra (Fig. 11) of an Fe-MFI zeolite impregnated with  $(NH_4)_2HPO_4$ , a shift of the signal attributed to oligomeric Fe-species from 350 to 310 nm, as expected for Fe with phosphate in first coordination sphere [31], was observed. Furthermore, a change in redox properties seemed to apply. Fe-species reducible by hydrogen at about 540 °C in unpoisoned Fe-MFI catalysts seemed to be stabilised against reduction by phosphate addition (Fig. 12). According to Devadas [25], the reduction of  $Fe^{3+}$  species to  $Fe^{2+}$  takes place at about 480 °C and the peak at about 550 °C

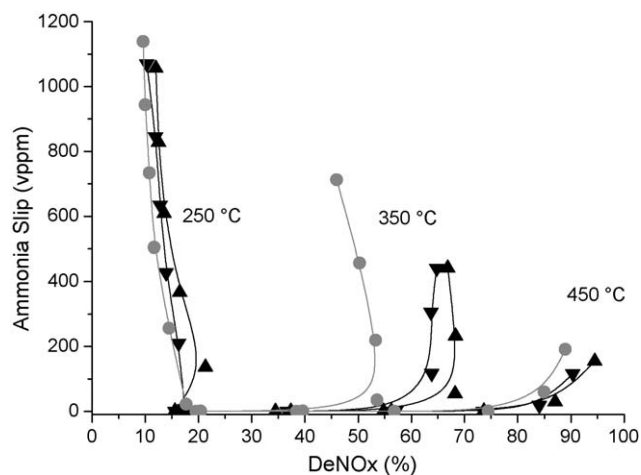


Fig. 10. Gas-phase poisoning of 400 cpsi Fe-MFI zeolite (90 g/L) honeycomb catalysts by phosphoric acid and zinc containing particulate. (▲) Fe-MFI catalyst hydrothermally treated (550 °C, 5 vol.%  $H_2O$ , air, 50 h, GHSV = 50,000  $h^{-1}$ ); (●) hydrothermal treatment + exposure to 3 mmol P from thermal decomposition of  $(NH_4)_2HPO_4$ ; P-content 0.6 wt.%, (▼) hydrothermal treatment + exposure to 3 mmol Zn from thermal decomposition of  $Zn(NO_3)_2$ ; Zn-content 0.15 wt.%, 1000 vppm NO, 200–1200 vppm  $NH_3$  ( $\alpha = 0.2, 0.4, 0.6, 0.8, 1, 1.2$ ), 1000 vppm CO, 5 vol.%  $CO_2$ , 5 vol.%  $H_2O$ ,  $N_2$ , GHSV = 50,000  $h^{-1}$ .

**Table 4**Characterization data of Fe–MFI zeolites poisoned with  $(\text{NH}_4)_2\text{HPO}_4/\text{Zn}(\text{NO}_3)_2$ .

Catalyst: Fe–MFI	$T_{50,\text{NO}}^a$ (°C)	$\text{NH}_3$ chemisorbed <sup>b</sup> [nmL/g]	$\text{NO}_2$ chemisorbed <sup>b</sup> [nmL/g]	BET surface <sup>c</sup> [m <sup>2</sup> /g]	Micropore surf. area <sup>c</sup> [m <sup>2</sup> /g]
Unpoisoned <sup>d</sup>	290	11.5 ± 1	2.6	308	525
1 wt.% P <sup>d</sup>	315	10	2.0	n.a.	n.a.
2.2 wt.% P <sup>d</sup>	325	10.5	1.1	263	< 445
0.3 mmol Zn/g <sup>d</sup>	335	11.5	n.a.	221	< 306

<sup>a</sup> Quartz glass laboratory flow reactor, packed bed, 75 mg catalyst ( $d_{\text{Grain}} = 100 \text{ nm} - 10 \mu\text{m}$ ), 500 mg SiC, volume flow: 700 mL/min, 1000 vppm NO, 1000 vppm  $\text{NH}_3$ , 7 vol.%  $\text{O}_2$ ,  $\text{N}_2$ .<sup>b</sup> Integration of TPD-concentration profiles after saturation at 150 °C.<sup>c</sup>  $\text{N}_2$  physisorption, BET analysis and Horvath–Kavazoe analysis.<sup>d</sup> Incipient wetness using water or aq. precursor solution ( $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{Zn}(\text{NO}_3)_2$ ) of the poison; then calcined in air (550 °C/24 h).**Table 5**Activity of a HCl treated 400 cpsi Fe–MFI (90 g/L) honeycomb SCR catalyst at  $\alpha = 1$  and 25 ppm  $\text{NH}_3$  slip.

Catalyst	DeNOx at 250 °C		DeNOx at 350 °C		DeNOx at 450 °C	
	$\alpha = 1$	$\text{NH}_3$ slip: 25 ppm	$\alpha = 1$	$\text{NH}_3$ slip: 25 ppm	$\alpha = 1$	$\text{NH}_3$ slip: 25 ppm
Hydrothermally treated	12%	17%	68%	68%	87%	86%
Hydrothermally treated + 3 mmol HCl	11%	16%	57%	66%	89%	90%

corresponds to the reduction of  $\text{Fe}^{2+}$  to  $\text{Fe}^0$ . Phosphate addition seemed to render parts of iron species irreducible, i.e. by plugging of micropores and further to stabilise Fe-species against reduction to  $\text{Fe}^0$  (peak at about 700 °C). As the rate determining step of SCR of NO to nitrogen is, at least at low temperatures, considered to consist of the oxidation of nitrogen monoxide to nitrogen dioxide by oxidic Fe-species, a stabilisation against reduction due to a direct interaction with phosphates should impact the activity.

While loss of active surface should be considered the predominant cause for deactivation of phosphorous poisoned Fe-zeolite catalysts, a direct interaction of active Fe-species with phosphates cannot be excluded and might add to observed activity losses.

### 3.5. Additives without significant influence on the catalytic properties of Fe-zeolites

Within the range of the experimental error, aluminium, cerium, and chlorides were found to have only a negligible effect to the catalytic properties of Fe-zeolite-based  $\text{NH}_3$ -SCR catalysts. A slight promoting effect of a wet-chemical impregnation of the over-exchanged zeolite with Ce(III)nitrate seemed to apply at a temperature of 350 °C, where, at low conversions (see Table 1), the reaction rate should mainly be controlled by the intrinsic

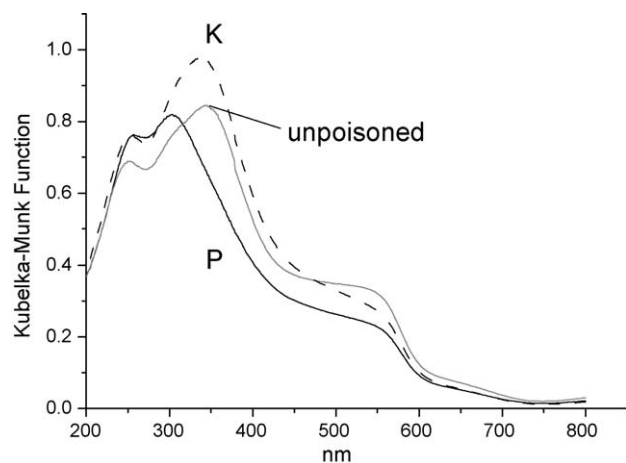
chemical kinetics. This was the case for both the Fe-BEA- and the Fe-MFI-zeolite, though a considerable scattering was observed in the data.

The low impact of chlorides was verified by poisoning of a Fe-MFI 400 cpsi (15 cm<sup>3</sup>, 90 g/L) honeycomb with HCl from the gas phase, the latter formed by thermal decomposition of  $\text{NH}_4\text{Cl}$ . A notable loss of DeNOx activity by exposure to hydrochloric acid was observed at 350 °C only, and only in case of ammonia excess ( $\alpha = 1, 1.2$ ). Note that reversible deactivation by formation of  $\text{NH}_4\text{Cl}$  is, due to the ex situ poisoning procedure, is not self-evident, but could be used as an explanation for activity losses observed in ammonia excess only.

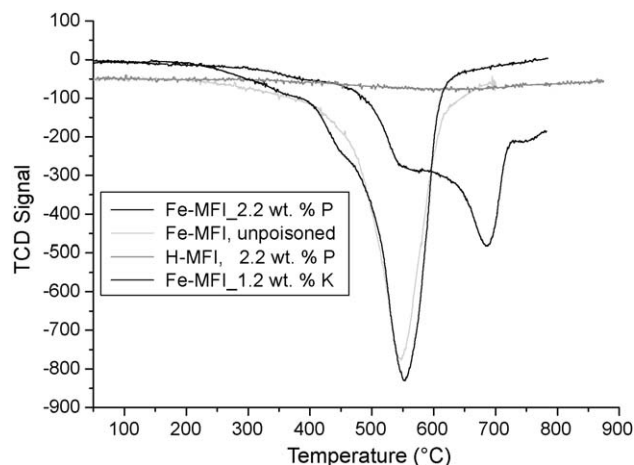
At the applied conditions at the automotive aftertreatment system (ammonia slip 10–25 vppm), the HCl treated catalyst retained its activity (Table 5). Chlorine induced dealumination of the zeolite may still present a risk for activity losses if the catalyst is operated at temperatures higher than 600 °C.

### 3.6. Further results from high-throughput experimentation, deactivating effects of inorganic additives to Fe-BEA-SCR catalysts

Due to the use of high-throughput experimentation techniques large amounts of data regarding activity losses of Fe-Zeolite SCR



**Fig. 11.** UV-vis-DRS spectra of Fe-MFI zeolites impregnated with water or aqueous solution of  $(\text{NH}_4)_2\text{HPO}_4/\text{KNO}_3$  to contain 2.2 wt.% P/1.2 wt.% K (0.3 mmol/g<sub>cat</sub>), then thermally treated (24 h, 550 °C, air).



**Fig. 12.**  $\text{H}_2$ -TPR profiles of Fe-MFI zeolites impregnated with water or aqueous solution of  $(\text{NH}_4)_2\text{HPO}_4/\text{KNO}_3$  to contain 2.2 wt.% P/1.2 wt.% K (0.3 mmol/g<sub>cat</sub>), then thermally treated (24 h, 550 °C, air).



**Table 6**

Deactivation of Fe-BEA SCR catalysts in high-throughput experiments (selected results).

Catalyst	Y <sub>N<sub>2</sub></sub> (%)		Y <sub>N<sub>2</sub></sub> (%) poisoned/Y <sub>N<sub>2</sub></sub> (%) unpoisoned	
	350 °C	450 °C	350 °C	450 °C
Fe-BEA/1 wt.% Na (0.45 mmol Na/g cat.)	3.5 ± 1	6 ± 2	0.14	0.1
Fe-BEA/0.2 wt.% K (0.05 mmol K/g cat.)	21 ± 2	45 ± 4	0.81	0.77
Fe-BEA/1 wt.% K (0.26 mmol K/g cat.)	10 ± 2	19.5 ± 3	0.36	0.34
Fe-BEA/0.5 wt.% Ca (0.125 mmol Ca/g cat.)	17 ± 3	44 ± 2	0.66	0.76
Fe-BEA/1 wt.% Ca (0.25 mmol Ca/g cat.)	7 ± 1	27 ± 3	0.3	0.46
Fe-BEA/1 wt.% Mg (0.41 mmol Mg/g cat.)	0	3	–	0.03
Fe-MFI/0.5 wt.% P (0.16 mmol P/g cat.)	21 ± 3	49 ± 5	0.81	0.84
Fe-MFI/1 wt.% P (0.32 mmol P/g cat.)	9 ± 1	22 ± 3	0.3	0.38
Fe-MFI/1 wt.% Zn (0.15 mmol Zn/g cat.)	5 ± 2	18 ± 2	0.21	0.31

catalysts have been accumulated. As apparent from data given above, different to studies with V-based catalysts [28] no combinatorial strategy was applied. The data presented above comprise a selection of results from “one at a time” variations of catalyst loadings, investigation temperature and the variation of the zeolite framework type. The relative deactivating effects of inorganic additives described above were further confirmed by experiments with Fe-BEA-SCR catalysts. A selection of results from high-throughput experiments with Fe-BEA catalysts with the same Fe-loading and Si/Al ratio as the Fe-MFI catalyst described above is given in Table 6.

#### 4. Conclusions

The poisonous potential of inorganic compounds to Fe-zeolite-SCR catalysts has been evaluated by high-throughput experiments and, for identified poisons, verified by poisoning substrates close to industrial application from the gas phase.

In the literature, chemical deactivation of Fe-zeolites has been suggested to be close to phenomena observed with vanadia-based SCR catalysts [16], thus said alkaline metals being strong poisons to the catalyst. While alkaline metals and alkaline earths exhibit deactivating potential towards Fe-zeolite catalysts, their resistance towards these poisons was shown to be much higher than that of a standard V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub>-SCR catalyst as currently used for NO<sub>x</sub> abatement in heavy duty applications. If high alkaline metal contents are to be expected in an exhaust stream (use of bio-diesel), the use of Fe-zeolites instead of vanadia-based materials is to be recommended. While the observed deactivation of Fe-zeolites by alkaline metals is influenced by the reduced acidity and ammonia storage capacity of the material, the predominant deactivation mechanism seems to be pore plugging by free poisons and/or micropore narrowing due to the uptake of metals with alkaline character on cationic positions.

Inorganics derived from the combustion of lubricant oil additives (P, Zn, B) present a further strong risk for activity losses of Fe-zeolite-based SCR catalysts. While the impact of zinc is, as with alkaline earths, mainly related to losses of active surface, a direct interaction of phosphates with Fe-species of low molecular weight cannot be ruled out and potentially contributes to observed activity losses.

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